The Critical Properties of Five Thermally Unstable Substances

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The critical constants $(T_c, P_c \text{ and } V_c)$ are key parameters in the prediction of thermodynamic and transport properties by the principle of corresponding states.

However, experimental determination of the critical property of unstable substances has proved difficult and subject to high uncertainty, because of thermal decomposition and other reactions near the critical point of such substances.

In this paper, a new method was developed for measurement of the critical temperatures and pressures of thermally unstable substances, in which a thick wall borosilicate glass tube contains the sample, and a plating of quartz glass is the heater. The short residence time at elevated temperatures minimizes decomposition and other reactions, making it possible to measure the critical properties of many unstable fluids. The advantage of the measuring apparatus was that a small amount of sample was sufficient to determine the critical properties accurately, and very short time was need to heat the sample uniformly. The apparent critical temperatures and pressures of five substances were obtained as a function of the heating time, and these have been extrapolated to the critical temperature and pressure of an undecomposed substance. The uncertainties of the critical properties measured in this work were ± 0.28 K in temperature, ± 0.02 MPa in pressure respectively.